An Investigation of the Chemical States
of Copper in Methanol Catalysts and Their
Relevance to Activity Maintenance

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Summary

Information on the chemical states of a catalyst surface is obtainable by X-Ray
Photoelectron Spectroscopy (XPS).   Copper-zinc oxide catalysts from the DOE
sponsored Liquid Phase Methanol (LPMeOH) project have been studied to ascertain
the oxidation states of copper on fresh, reduced, and spent catalyst samples.
Using the Auger parameter to differentiate valence levels it is shown that Cu^{+1}
must be maintained on the surface for continued catalyst activity to methanol.
Unusually strong shifts, due to matrix effects, in the $Cu2p_{3/2}$ binding energy
for reduced/active catalysts indicate that Cu^{+1} is stabilized by incorporation
within the ZnO lattice.   Energy Dispersive X-Ray Spectrometry (EDS) and XPS show
that while the bulk Cu/Zn ratio is maintained at a value near 2.1 the surface
Cu/Zn ratio decreases in use to well below unity.   The effects of metal and
halogen poisoning have also been studied by the additions of iron (as iron
carbonyl) and chlorine, and are observed to deactivate the catalyst by reduction
of Cu^{+1} to Cu^0.   These results suggest a relationship between the copper state
needed to maintain activity and the reducing/oxidizing potential of the reactant
gases.

Introduction

Determination of the active copper state in copper/zinc/alumina catalysts, used
for methanol synthesis, has been of recent interest (1-5). Klier and coworkers,
using optical spectroscopy, have presented evidence indicating Cu^{+1}, dissolved
in the ZnO lattice(1,2), as the catalytically active state.   X-Ray Photoelectron
Spectroscopy (XPS) has been employed by Okamato et al.(3,4) to show that CuO-ZnO
samples containing less than 10% copper, upon reduction, do exhibit weak Cu(LMM)
x-ray induced Auger lines suggestive of the presence of Cu^{+1}.   The Okamato
studies, unfortunately, do not present supporting data regarding activity of the
catalysts to methanol synthesis. Himelfarb et al.(5) have presented evidence, by
X-Ray Diffraction (XRD), for the existence of an intermediate Cu^{+1} phase during
reduction of copper-zinc oxide catalysts.   Since XRD is a bulk sensitive technique
the chemical state of the surface is, however, still in doubt.

In conjunction with the current DOE sponsored Liquid Phase Methanol Project
(LPMeOH) we have undertaken studies of commercially available copper-zinc oxide
catalysts which have demonstrated actual activity to methanol synthesis in both
the gas and liquid phases. Here we present XPS results which confirm that Cu^{+1}
is indeed the active state.   Poisoning by metal and/or halogens has also been
investigated by XPS and Energy Dispersive X-Ray Spectrometry (EDS). Deactivation
apparently occurs via reduction of Cu^{+1} to Cu^0.

Because the chemical shifts observed in the XPS spectrum for copper are limited it
is necessary to employ the Auger parameter to follow the three valence states
Cu^0, Cu^{+1}, and Cu^{+2}.   The Auger parameter (α), proposed by Wagner(6) and
later modified by Gaarenstrom and Winograd(7) is defined as:

$$\alpha + h\nu = BE_p + KE_A = \alpha' \qquad 1)$$

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where $h\nu$ is the photon energy, BE_p the binding energy of the photoelectron peak, and KE_A the kinetic energy of the x-ray induced Auger line which is also observed in the spectrum. The addition of $h\nu$ to α is defined as α', the modified parameter(7), and is independent of the excitation energy.

From Equation 1 a plot of α' vs the corrected BE_p can be generated. This plot or Auger map, as it is referred, enables one, through analyses of standards, to assign regions to a particular elemental oxidation state or chemical environment.

Experimental

A commercially available copper-zinc oxide catalyst, in powdered form (2-7μm), has been used in these studies. Gas phase and in situ liquid phase reductions were performed by suitable laboratory adaptation of the commercial gas phase technique. Catalysts from liquid phase studies were prepared for surface analysis by stripping the inert oil via a series of cyclohexane washings in a nitrogen filled glove box. Upon drying, the samples were transported to an argon filled glove box. The catalyst samples were applied to a piece of double-sided adhesive tape attached to a sample mount. The mounts were then sealed in a vessel for transportation to the spectrometer. Under vacuum the vessels were reopened and the mounts attached to the transfer rod assembly.

XPS has been performed on a Physical Electronics 560 spectrometer equipped to perform XPS, Scanning Auger Microscopy (SAM), Ion Scattering Spectroscopy (ISS), and Secondary Ion Mass Spectrometry (SIMS). Mg Kα radiation (1253.6eV) at 15 keV and 20mA was used as the excitation source. Charge correction was performed by referencing to the $Zn2p_{3/2}$ line at 1021.7eV and C1s, for residual oil, at 284.7eV. Both lines were found to agree to within $\pm$ 0.2eV.

EDS was performed on an Amray 1000 Scanning Electron Microscope (SEM) equipped with a Kevex 7000 spectrometer. Quantitative analysis was accomplished using ZAF corrections.

Copper oxide standards were prepared in situ by mounting a cleaned and polished (to 1μm alumina) copper foil to a probe that could be heated and cooled. After repeated cycles of ion sputtering and annealing at 300°C, a clean surface was obtained as verified by Auger Electron Spectroscopy (AES) and XPS. A thin film of CuO was then produced on the surface by heating the foil to 250°C under a stream of air. Larson(8) has reported that Cu_2O can be produced by reheating the CuO surface film to 250°C in vacuum. The advantage of this preparation is that surface charging is negligible due to the conduction of the thin oxide films produced on the surface.

Results and Discussion

Because of discrepancies in the literature(6,8), regarding the binding energy of the $Cu2p_{3/2}$ line, a study to determine α' for Cu, Cu_2O, and CuO was undertaken. The results of this investigation are listed in Table 1. The $Cu2p_{3/2}$ line is not observed to shift as copper metal is oxidized to Cu_2O, however, the Cu(LMM) line is found to move from 334.8eV to 336.8eV. This change causes a shift in α' from 1850.9eV, for copper metal, to 1848.9eV for Cu_2O. Further oxidation to CuO results in the $Cu2p_{3/2}$ line shifting to 933.2eV as well as the Cu(LMM) line to 335.6eV. The net result is a reshifting of α' back to 1851.2eV. These movements in α' are better illustrated by the Auger map, shown in Figure 1, which indicates the regions occupied by copper metal and its oxides. Though CuO and Cu metal possess the same α' value, the shift in the $Cu2p_{3/2}$ line, as well as the observation of satellites due to the paramagnetic nature of Cu^{+2} in the Cu2p spectrum, permits these chemical states to be distinguished.

The fresh, as received catalyst is found to be comprised of copper primarily as CuO. This is indicated by the observation of strong satellite peaks and an α' of 1851.0eV. Upon reduction, the Cu2p spectrum is observed to undergo a loss in satellite structure and a shift in the $Cu2p_{3/2}$ binding energy. Also, as shown in Table 1, the $Cu2p_{3/2}$ line is found to move from 933.6eV to 931.7eV. The x-ray induced Auger line, however, remains at 336.2eV. Calculating α' shows that the Cu^{+2} has been reduced to Cu^{+1}. To better illustrate these observed changes the Auger map is depicted in Figure 2. The region occupied by the reduced catalyst is in good agreement with the coordinates for Cu_2O in Figure 1. Thus it appears that Cu^{+1} is present on the surface after reduction. The binding energy shift observed for the $Cu2p_{3/2}$ line as the copper is reduced is observed to be significantly greater than expected for Cu^{+2} being reduced to the Cu^{+1} state. For Cu_2O, the $Cu2p_{3/2}$ line is found to be at 932.1eV while for the reduced sample a shift to 931.7eV is observed. This larger than anticipated chemical shift is believed to be attributable to matrix effects, similar to those observed by Kim and Winograd for Au implanted in SiO_2(9). The Cu^{+1} is apparently stabilized on the surface by its incorporation within ZnO lattice defects.(2) The electron rich environment offered by these sites is thus believed responsible for the large shift in the $Cu2p_{3/2}$ binding energy. In as received form (oxide), elemental analysis shows a Cu/Zn ratio of approximately 2 to 1. XPS measurements, however, clearly and reproducibly show a surface Cu/Zn ratio of almost unity.

After reduction the catalysts are used to produce methanol in either gas or liquid phase operations. Upon demonstration of satisfactory activity, samples of the catalysts are removed for analysis. In Table 1 and Figure 2 the results of studies on these active catalysts are also shown. The copper present on the surface is observed to exist as Cu^{+1} by the fact that α' remains at 1849.0eV. The surface Cu/Zn ratio, calculated by XPS, is found to decrease to approximately 0.7 to 1 upon reduction. This ratio becomes even smaller (0.3 – 0.1) after use in the reactor.

Upon an observed loss in activity a catalyst sample was again removed for analysis. The data, shown in Table 1 and Figure 2, indicates that Cu^{+1} has been reduced to Cu^0 by the observation of a shift in α' to 1851.0eV. It is our contention that deactivation is occurring by the reduction of Cu^{+1} to Cu^0 on the surface. this suggests that the continued presence of Cu^{+1} is important in maintaining catalytic activity.

The small particle size (2-7μm) of the catalyst powder used in liquid phase operations has permitted the use of EDS to rapidly determine a bulk Cu/Zn ratio for comparison with the surface ratio obtained by XPS. The results indicate that while the bulk Cu/Zn ratio remains at 2.1, a decrease in the surface Cu/Zn ratio, calculated by XPS, is observed upon reduction and use. Catalyst reduction decreases the surface Cu/Zn ratio from 1.0 to ~0.7. After use in methanol synthesis this ratio is found to further decrease to values approaching 0.3. This data fits well with proposals by Klier and coworkers(2) regarding specific site stabilization of Cu^{+1}. Since only a finite number of defect sites are anticipated within the ZnO lattice near the surface the Cu/Zn ratio is expected to decrease as Cu^{+1} dissolves within the ZnO lattice. Therefore recrystallization, due to excessive heat, is expected to severely effect the surface's ability to synthesize methanol. A requirement, for tight temperature control, thus is necessary to prevent surface recrystallization which suggests that the LPMeOH process offers significant advantages, as a result more efficient heat transfer, over gas phase synthesis.

Poisoning and its effects upon surface copper have also been investigated. The injection of a very low level of $Fe(CO)_5$ to the feed stream is observed to cause

a rapid deactivation of the catalyst. XPS indicates that no iron is apparently present on the surface of these samples. EDS analysis, however, shows that iron is present in the bulk of the poisoned samples. By XPS changes in the Cu(LMM) spectrum are observed. In Figure 3, the Cu(LMM) spectra for a fresh-reduced catalyst is compared with that obtained after iron poisoning. The observation of a second peak near 334.6eV is attributed to the presence of Cu^0 on the surface. Using Equation 1, α' is found to be equal to 1851.0eV for this new line. This region has been earlier determined, in the oxide study, to be occupied by metallic copper (Fig. 1). Thus upon contact with iron the Cu^{+1} is reduced to Cu^0, thereby deactivating the catalyst. Chlorine poisoning has also been investigated and the chlorine, likewise, appears to deactivate by reducing the surface Cu^{+1} to Cu^0. Unlike iron poisoning, XPS and EDS are both able to detect the presence of chlorine on the surface as well as a reduction in the Cu/Zn ratio at the catalyst surface. The mechanisms of deactivation are not well understood at this time and are currently the subject of continued research.

Conclusion

From this study it has been determined, using the Auger parameter, that Cu^{+1} is the active chemical state of copper on the surface, and is apparently stabilized by its incorporation within the ZnO lattice. Deactivation is believed to occur by the reduction of Cu^{+1} to Cu^0. Poisoning by either Fe or Cl is observed to also proceed through a mechanism by which the Cu^{+1} is reduced to Cu^0.

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Table 1

Results of Copper Auger Parameter
Determination for Copper Oxide Standards and
Catalyst Samples Analyzed by XPS

Sample	$Cu2p_{3/2}$(ev)[1]	$Cu(LMM)$(eV)[2]	α'(ev)
Clean Cu	932.1	334.8	1850.9
Cu_2O	932.1	336.8	1848.9
CuO	933.2	335.6	1851.2
Fresh-Unreduced Catalyst	933.6	336.2	1851.0
Fresh-Reduced Catalyst	931.7	336.2	1849.1
Spent-Active Catalyst	931.9	336.5	1849.0
Spent-Deactivated Catalyst	932.0	336.6	1849.0
	932.0	334.6	1851.0

[1] $Cu2p_{3/2}$ energies presented as binding energies.
[2] $Cu(LMM)$ energies presented in this study as binding energies for consistency.
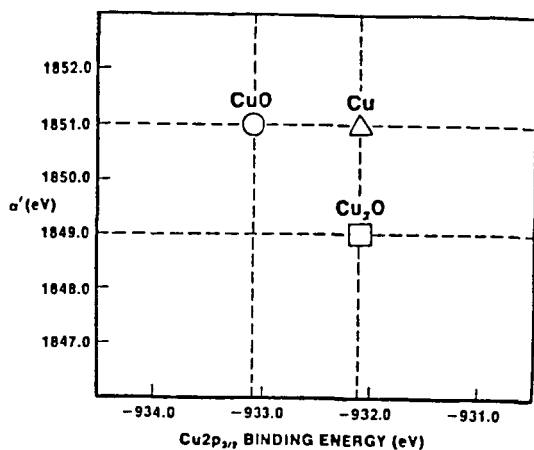
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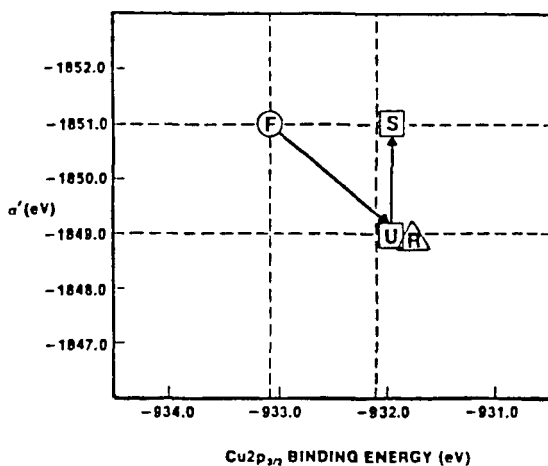Figure 1: Auger map depicting results of in situ copper oxide study.

Figure 2: Auger map illustrating the observed changes in the surface copper oxidation state for: (F) fresh-as received catalyst, (R) fresh-reduced catalyst, (U) methanol-active catalyst, and (S) spent catalyst.
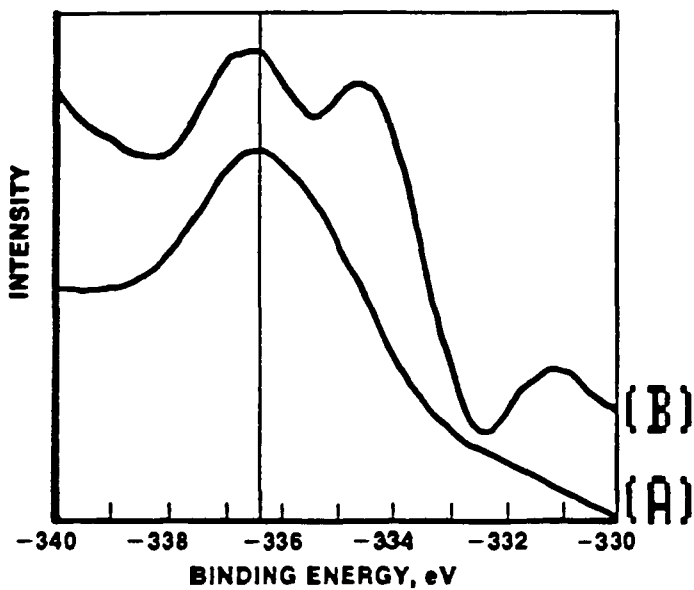
Figure 3: Cu(LMM) X-ray induced Auger spectra for (A) fresh, methanol-active catalyst and (B) spent catalyst.